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MODIFIERS FOR CEMENTITIOUS MATERIALS

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(56) Prior Art Documents

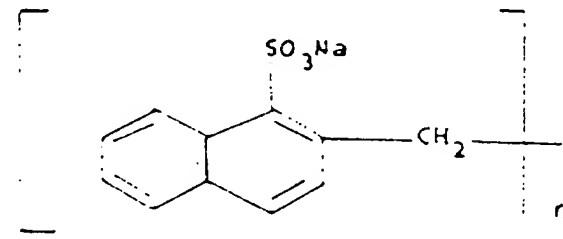
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US 3465825

(57) Claim

1. A modifier for cementitious mortars and the like comprising:-

70-80 parts by weight of hydroxy propyl methyl cellulose,

10-40 parts by weight of a sodium salt of a naphthalene formaldehyde sulphonate having the general formula:



wherein n is from 2-10;

and a substantially chlorine free, non-aflame-retarding cement accelerator.

6. A modified cement mortar having the composition:-
1 part by volume of portland cement, 3-6 parts by volume of
sand, and 0.001-0.010 parts by volume of a modifier as
defined in any one of claims 1-5.

7. A method of modifying a cementitious mortar or the
like comprising mixing together the dry mortar ingredients
with 0.001-0.010 parts by weight of a dry powdered modifier
according to any one of claims 1-5 and subsequently adding
water to a desired consistency.



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AMENDED

APPLICATION FOR A PATENT

We, A.V. SYNTech PTY. LTD.

572111

of 27 Edgar Street, Northgate, 4013, Queensland, Australia

hereby apply for the grant of a Patent for an invention entitled:

MODIFIERS FOR CEMENTITIOUS MATERIALS

which is described in the accompanying Provisional ~~Complex~~ Specification.

Our address for service is: C/- G.R. Cullen & Company, Patent Attorneys, of
Medibank Building, 82 Ann Street, Brisbane, in the state of Queensland,
Commonwealth of Australia.

DATED this Third day of May 1985

ATTACHMENT SHEET AND AMENDMENTS

11000 7-2-88

A.V. SYNTech PTY. LTD.
By its Patent Attorneys
G.R. CULLEN & COMPANY.

Peter C. Fisher.

To:

The Commissioner of Patents,
Commonwealth of Australia.

COMMONWEALTH OF AUSTRALIA
THE PATENTS ACT 1974

DECLARATION IN SUPPORT OF AN
APPLICATION FOR A PATENT

In support of the Application made for a patent
for an invention entitled:

"MODIFIERS FOR CEMENTITIOUS MATERIAL"

Insert
Title of Invention

Insert
Full Name(s) and
Address(es)

I/We Michael John MARTIN

of 2 Neulands Road, INDOOROOPILLY, 4068, Brisbane,
Queensland, Australia,
do solemnly and sincerely declare as follows:-

Insert
Full Name(s) of
Applicant(s)

1. I am/We are the applicant(s) for the patent -
(or, in the case of an application by a body corporate)

1. I am/We are authorised by SYNTEC CHEMICALS PTY. LTD.

the applicant(s) for the patent to make this declaration on its behalf.

2. I am/We are the actual inventor(s) of the invention referred to in the basic
application(s)

~~and no other person has any interest in the invention(s).~~

Full Name(s) and
Address(es) of
Inventor(s)

X

State how Applicant(s)
derive title from inventor(s)
e.g. The Applicant(s)
is/are the assignee(s) of the
invention from the
inventor(s)

~~is/are the actual inventor(s) of the invention and the facts upon which the applicant(s)~~
~~is/are entitled to make the application are as follows:-~~

The said Applicant, Syntec Chemicals Pty. Ltd.
is the Assignee of the said invention from the
said actual Inventor, Michael John Martin.

*Note: Paragraphs
3 and 4 need only be
completed for a
Convention Application

Basic Country(ies)
Priority Date(s)
Basic Applicant(s)

3. The basic application(s) as defined by Section 141 of the Act was/were made

in on
by
in on
by

4. The basic application(s) referred to in paragraph 2 of this Declaration was/were
the first application(s) made in a Convention country in respect of the invention(s)
the subject of the application.

Declared at Brisbane this 27 day of May 1984

To: The Commissioner of Patents

G. R. CULLEN & COMPANY

Signature of Declarant(s)
M.J. Martin, DIRECTOR

572111

23766/54

COMMONWEALTH OF AUSTRALIA

The Patents Act 1952-1969



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COMPLETE SPECIFICATION FOR THE INVENTION ENTITLED:

"MODIFIERS FOR CEMENTITIOUS MATERIALS"

The following statement is a full description of the invention
including the best method of performing it known to us:

- 2 -

This invention is concerned with the addition of
reinforcing materials such as calcium aluminate cement
to improve certain properties thereof.

The invention is concerned generally with, but
not exclusively, with modifiers for cementitious mortars
workability and strength characteristics.

Most cement mixtures used for masonry, tiles and
concrete blocks comprise 1 part by volume cement, 1.5 parts
10 1 part fine aggregate and 3-6 parts water.

High strength mortars ideally have only sufficient
water added to the mix to hydrate the cement by weight water
present during hydration substantially limitlessly thus all
the ultimate properties of the cured mortar. A major
15 difficulty of an "ideal" mortar containing an optimum water
content is that the mortar rapidly becomes stiff and loses
its "workability" as the cement hydrated. Addition of
bricklayers of extra water to soften the mix at this state
is often the cause of poor mortar performance particularly
20 in relation to compressive strength and tensile strength of the
cured mortar.

"Workability" of a cement mortar is a combination
of characteristics which relate to the degree of fluidity
of the wet mortar mix. A workable mortar has early
25 fluidity enabling ease of application to a course of tiles
or blocks and ease of bedding of a fresh block or block. At
the same time a workable mortar should lose its initial
fluidity and stiffen at a relatively short interval to
provide adequate support beneath a previously laid course.
30 Initial workability of a fresh mortar mix is assessed by
traditional means such as a slump test or flow and water
retention tests set forth in Australian Standard
No. AS1016 "Masonry Cement".

The workability of a mortar mix can be affected
35 seriously by high ambient temperature conditions which

increase moisture evaporation and cement hydration.

Another very important factor is the nature of the brick or block itself which can affect the workability of the mortar. Often this can have a seriously detrimental effect on the bond between the mortar and the brick or block. Accordingly, it is a requirement of the mortar to compensate for many variables including ambient temperature conditions as well as the properties of the brick or block in order to ensure optimum performance.

Although the requirements for cement mortars for brickwork and blockwork are set out in the Appendices to Australian Standards AS 1640 and AS 1478 respectively, in practice most bricklayers tend to mix and use mortars according to their own requirements rather than industry standard, inconvenience which may interfere with their laying rate. The result of this is that considerable inconsistency in mortar bond strengths will occur from batch to batch.

Of all the properties required of a good mortar mix, water retention is the most important as it is this property which has the most profound effect on bond strength.

"Water retention" is a standard measure of the property which enables a mortar to resist the "suction" exerted by a porous brick or block. Good water retention properties are important for three reasons: first, because water is prevented from bleeding out of the mortar; secondly, because the mortar bed is prevented from stiffening too much before the brick can be placed in position; and thirdly, because sufficient water is retained in the mortar to ensure proper hydration of the cement.

The SAA Codes for brickwork and blockwork both require a water retention value of at least 80% when tested in accordance with the method set forth in AS 1316. Briefly, the test involves a determination of mortar flow 35 before and after applying "suction" to the mortar for one

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minute.

Water Retention, $\omega' = \frac{\text{flow after 1 min}}{\text{flow before start}}$

The strength of the bond depends upon the bond between the brick and mortar depends inter alia, on the suction achieved between the absorption characteristics of the brick on one hand and the water retention characteristics of the mortar on the other.

For example, when bricks with weak absorption are combined with mortar with strong water retention, the bricks will "float" on the mortar bed. The effects of such a combination are that the mortar takes too long to stiffen or cure delaying construction and failure occurs at the interface with the result that the bond is poor.

If bricks with strong absorption are combined with mortar having poor water retention, the opposite effect will be observed. The mortar stiffens too rapidly and the next course of bricks cannot be tamped firmly. Further, the bricks may absorb sufficient water from the mortar that there is insufficient left to properly hydrate the cement. In any event, the bond is poor.

The standard measure of a brick's absorption characteristics, so far as they affect bond, is the initial rate of absorption (IRA). The IRA is the amount of water absorbed by a standard area of the bed face of the brick in one minute and is the property hitherto referred to as "suction".

Clay bricks, depending on the nature of the clay and the method of production are generally classified into three groups having high, intermediate and low IRA's. Generally speaking, clay bricks have an IRA in the range 0.2 - 6.5 kg m⁻²min⁻¹ whereas concrete bricks and blocks have an IRA in the range 0.7 - 1.5. The IRA of a brick or block will of course vary depending on the moisture content at the time of testing.

Thus it can be seen that there are many variations

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to be taken into account in mixing of mortars for a particular brick or block laying operation. Many of these variables give rise to contradictory requirements.

In an endeavour to provide high quality mortar with consistent properties it is possible to chemically modify the mortar.

Workability problems in the use of mortar mixes may be overcome to some degree by the use of certain additives which may be broadly categorized into:

- 10 i) water retaining agents
- ii) water reducing agents
- iii) accelerators
- iv) retardants.

The most commonly used water retaining agent is a carboxy methyl cellulose - CMC which finds its use or application in cement mortars applied to bricks or blocks with a high rate of initial absorption such as Calcium Silicate bricks. CMC is difficult to dissolve in water at ambient temperatures and may give rise to an uncontrolled stiffening of the mortar during mixing. When mixed with a cement mortar, conventional CMC additives are inclined to create an early stiffening of the mortar although if sufficient shear is applied to the mix a certain thin consistency may be noted. In general, the early stiffening is 20 disadvantageous and thus a retardant must be used to maintain workability. Of more recent times, a delayed solubility CMC has been used to avoid early stiffening but this does not overcome the problems of poor workability, particularly at low ambient temperatures.

30 Water reducing agents enable a reduction in the water/cement ratio at a given workability compared with an unmodified mortar and these are generally known as plasticizers.

Where a high rate of initial absorption is not a controlling factor, a plasticizer may be added to the mortar

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mix to increase the degree of fluidity thereof without the necessity of additional water.

The most commonly used plasticizers have specific functions and are chosen in accordance with the strength requirements of the cured mortar or "to frequently the conditions under which the mortar is to be used."

Plasticizers may be categorized as,

- A. Normal water reducing agents,
- B. Accelerating water reducers which will accelerate cement hydration under ambient conditions.
- C. Retarding water reducing agents which retard cement hydration under ambient conditions.
- D. Air entraining agents which entrain microscopic air bubbles to reduce mortar viscosity, and
- E. Superplasticizers which enable massive additions thereof without the deleterious effects normally associated with excess concentrations of types A, B or C above.

When adding workability modifiers to batches of mortar, most laborers tend to guess the quantity required and tend to "overdose" the batch. Excess concentrations of additives A-D will almost invariably reduce mortar quality.

The most widely used modifier in cement mortars is hydrated lime which extends mortar workability by its retardant effect. In addition, bricklayers prefer to use "bricklayers sand" instead of washed, sharp beach or river sand recommended for its superior strength qualities. "Bricklayers sand" contains a certain amount of clay or other micro-fine impurities which improve the workability of a mortar mix but is known to have deleterious effects on the mechanical properties and bond strength of a cured mortar. Hydrated lime is relatively expensive and has the serious disadvantage of contributing to unsightly efflorescence of calcium salts on finished clay brick or

concrete block masonry.

Typical water reducing agents are exemplified as follows:

Normal	Purified lignosulphonate, lignosulphonate + air-entraining agent, hydroxy-carboxylic acid at low dosage, hydroxylated polymer at low dosage.
5 Accelerating	Lignosulphonate + CaCl_2 , lignosulphonate + triethanolamine, lignosulphonate + Ca formate , hydroxy-carboxylic acid + CaCl_2 .
10 Retarding	High sugar lignosulphonate, hydroxy-carboxylic acid, hydroxylated polymer.
Air-Entraining	Impure lignosulphonate, lignosulphonate + surfactant, hydroxy-carboxylic acid + surfactant.
15 Superplasticizers	Pure lignosulphonate, salt of formaldehyde-naphthalene sulphonate, salt of formaldehyde-melamine sulphonate.

20 Of these compositions, all, with the exception of certain naphthalene formaldehyde sulphonates possess one or more serious disadvantages in additives in cement mortars. These disadvantages include high cost, variable quality and/or undesirable accelerating, retarding or air entrainment properties which require addition of further modifiers to control ultimate cured mortar properties.

The composition and mechanism of accelerators and retardants is well known in the cement and concrete art and thus will be dealt with only briefly in this document.

30 Accelerators are usually chosen from calcium chloride, calcium formate and triethanolamine and are used to accelerate hydration of cement, often in conjunction with a plasticizer having retardant properties. Of these accelerators, calcium formate is the only readily water soluble, dry powder with stable storage properties.

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Calcium formate, unlike other accelerators does not contribute to corrosion of reinforcing steels or cause efflorescence.

Most of the plasticizers when used alone in cement mortars act as retardants although polysaccharide polymers may be used for this purpose.

From the foregoing comments it will be clear that it is virtually impossible for the average admixture to modify the workability of an 'optimum' cement mortar without incurring some deleterious side effect in the cured mortar properties.

It is an aim of the present invention to overcome or alleviate the problems of prior art workability modifiers for concrete and cementitious mortars and at the same time provide enhanced physical and mechanical properties in the cured concrete and cementitious mortars.

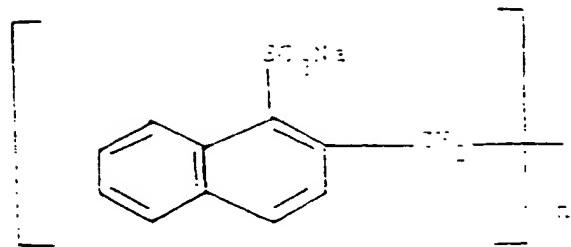
According to one aspect of the present invention there is provided a modifier for cementitious materials comprising:-

20 70-30 parts by weight of hydroxy propyl methyl cellulose,

10 10-40 parts by weight of a sodium salt of a naphthalene formaldehyde sulphonate having the general formula:

AMZ

- 8a -



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wherein n is from 2-10;

and a substantially chlorine free, non-efflorescing cement
accelerator.

Preferably said hydroxy propyl methyl cellulose has

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- 3 -

a molecular weight of from 60,000 - 120,000.

Preferably said modifier comprises a dry powder readily soluble in water at ambient temperatures.

According to another aspect of the present
5 invention there is provided a modified cement mortar having
the composition:-

1 part by volume of portland cement
3-6 parts by volume of sand and
0.001-0.010 parts by volume of a modifier as
10 described above.

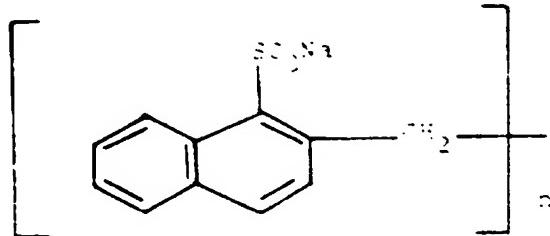
A preferred embodiment of the invention will now be described with reference to the following examples.

EXAMPLE 1 Modifier

The modifier preferably comprises a dry powder
15 having the following composition:-

(a) 66.6 parts by weight of hydroxy propyl methyl cellulose having a molecular weight in the range 85,000 - 95,000;

20 (b) 26.74 parts by weight of a sodium salt of naphthalene formaldehyde sulphonate of the general formula:



25

wherein n is 7-10.

(c) 6.66 parts by weight of calcium formate.
30 Each of the dry powder ingredients is mixed together in the above proportions in any suitable powder mixer e.g., a ribbon blander, drum tumbler, high speed blade mixer etc. in either a batch or continuous manner. The dry powder mixture is then packed into suitable containers for storage, shipping and dispensing. Most suitably the powder
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ixture is packed into dispensers adapted to hold the portions of predetermined quantities.

EXAMPLE 2 Mortar

5 A mortar comprising 1 part by volume of ordinary cement and 5 parts by volume of clean washed sharp sand was mixed in a cement mixer. 0.001 parts by volume of the powder modifier of EXAMPLE 1 was added to the mortar at the commencement of the mixing cycle.

10 The bond strength of the mortar was then tested on clay bricks and concrete blocks in accordance with AS 1640 and AS 1476 respectively. In both test methods, bond strength is determined by bending tests carried out on piers tested at the two ends and loaded as specified in the relative Standard.

15 The bending test is illustrated with reference to AS 1640 in FIG. 1 wherein a pier comprising nine clay bricks 1 bonded together with mortar 2 between the bricks is supported at each end by further bricks 3. The pier is then loaded by carefully stacking bricks 4 on the centre 20 three bricks 1 until the beam breaks.

The modulus of rupture (bond strength) is determined from $\frac{M}{Z}$ (MPa)
where M = central bending moment at failure in newton millimetres (N.mm)

$$25 \quad M = 1.23 W_1 L + 1.63 W_2 L$$

$$W_1 = \text{effective mass of the beam in kilograms} \\ = \frac{n-z}{n-1} W$$

where W = actual mass of beam (kg)
 n = number of courses in pier

30 W_2 = mass of load (kg)

L = clear span (mm)

Z = section modulus of the pier (mm^3).

Bond strength may also be tested as bond in shear as provided by the relevant Standards. Comparative results are shown in the Table in FIG. 2 from which it can be seen that for concrete blocks in particular, bond

Appendix A further defines the invention which the invention may be implemented without departing from the spirit compared with unmodified mortars.

In use the laying of masonry units such as concrete blocks, the modified mortar has the advantage of workability, for given ambient conditions, of unmodified mortars in general. Thus, when the masonry blocks are bedded in the modified mortar, that despite the extended workability, the blocks are readily seated, and the joints are made such that successive courses of masonry may be built up at normal or higher than normal rates.

Even under extremely adverse conditions of high ambient temperatures and humidity, with a correspondingly rapid rate of absorption the workability, and the strength of the mortar remains substantially unaltered.

While the mechanism of the present invention is not clearly understood, mortars containing admixtures with the present invention have extended workability, in that they exhibit rapid hydration characteristics when a concrete block is bedded. This anomalous behavior is not only beneficial in the physical act of laying of clay, brick, concrete blocks and the like but is also accompanied by substantially improved physical, chemical and mechanical properties of the mortar itself.

The hydrated mortar has excellent compressive strength, reduced porosity and exhibits substantially no efflorescence. In short, mortars containing an admixture with the present invention exhibit none of the properties usually associated with mortars modified with the great art modifiers or modifier combinations.

It is anticipated that the present invention will be equally applicable to concrete for manufacture of other concrete products with similar resultant advantages. In particular the modifier according to the invention may be

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used in pumping of concrete to maintain workability and to prevent water separation. Addition of the modifier to cementitious renders or plasters assists workability and maintains a "wet edge" for subsequent edge joints.

5 It will be readily apparent to a skilled addressee that many variations or modifications may be made to the present invention without departing from the spirit and scope thereof.

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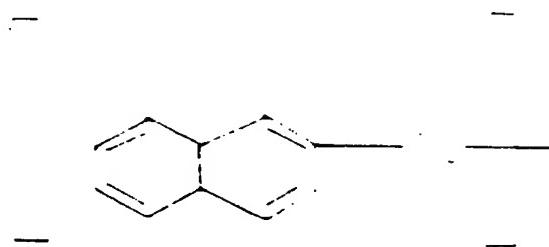
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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A modifier for cementitious mortars and like compositions comprising:

10-100 parts by weight of hydroxy propyl methyl cellulose,

11-40 parts by weight of a dry calcium formate naphthalene formulation having a formula in the following formula



wherein n is from 1-10
and a substantially chlorine free non efflorescent cement accelerator.

2. A modifier as claimed in claim 1 wherein said hydroxy propyl methyl cellulose has a molecular weight of from 60,000 - 100,000

3. A modifier as claimed in claim 1 or claim 2 wherein said modifier comprises a dry powder readily soluble in water at ambient temperatures

4. A modifier as claimed in any preceding claim wherein said accelerator comprises calcium formate

5. A modifier for cementitious mortars and like compositions comprising:

11-66 6 parts by weight of calcium formate

1/1

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methoxyl cellulose having a molecular weight in the range 35,000 - 95,000.

11. 26-74 parts by weight of a sodium salt of naphthalene formaldehyde sulfonate having the general formula:



wherein n is from 1-10.

12. 6-12 parts by weight of calcium formate.

13. A modified cement mortar having the composition: 1 part by volume of portland cement, 1.5 parts by volume of sand, and 1.00-1.05 parts by volume of a modifier as defined in any one of claims 1-6.

14. A method of modifying a cementitious mortar or the like comprising mixing together the dry mortar ingredients with 3.00-4.00 parts by weight of a dry powdered modifier according to any one of claims 1-6 and subsequently adding water to a desired consistency.

15. A modifier for cementitious mortars and the like substantially as hereinbefore described with reference to the examples.

DATED this Second Day of March, 1968

A. V. SYNTEZ PFK, LTD.
By its Patent Attorneys
G. R. CULLEN & CO.,

JL

FIG. 1

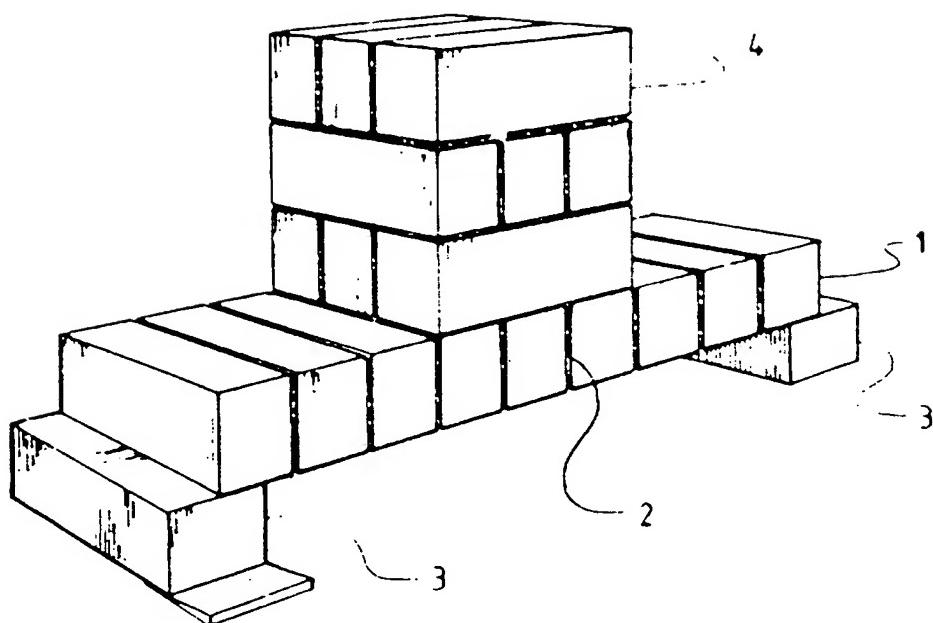
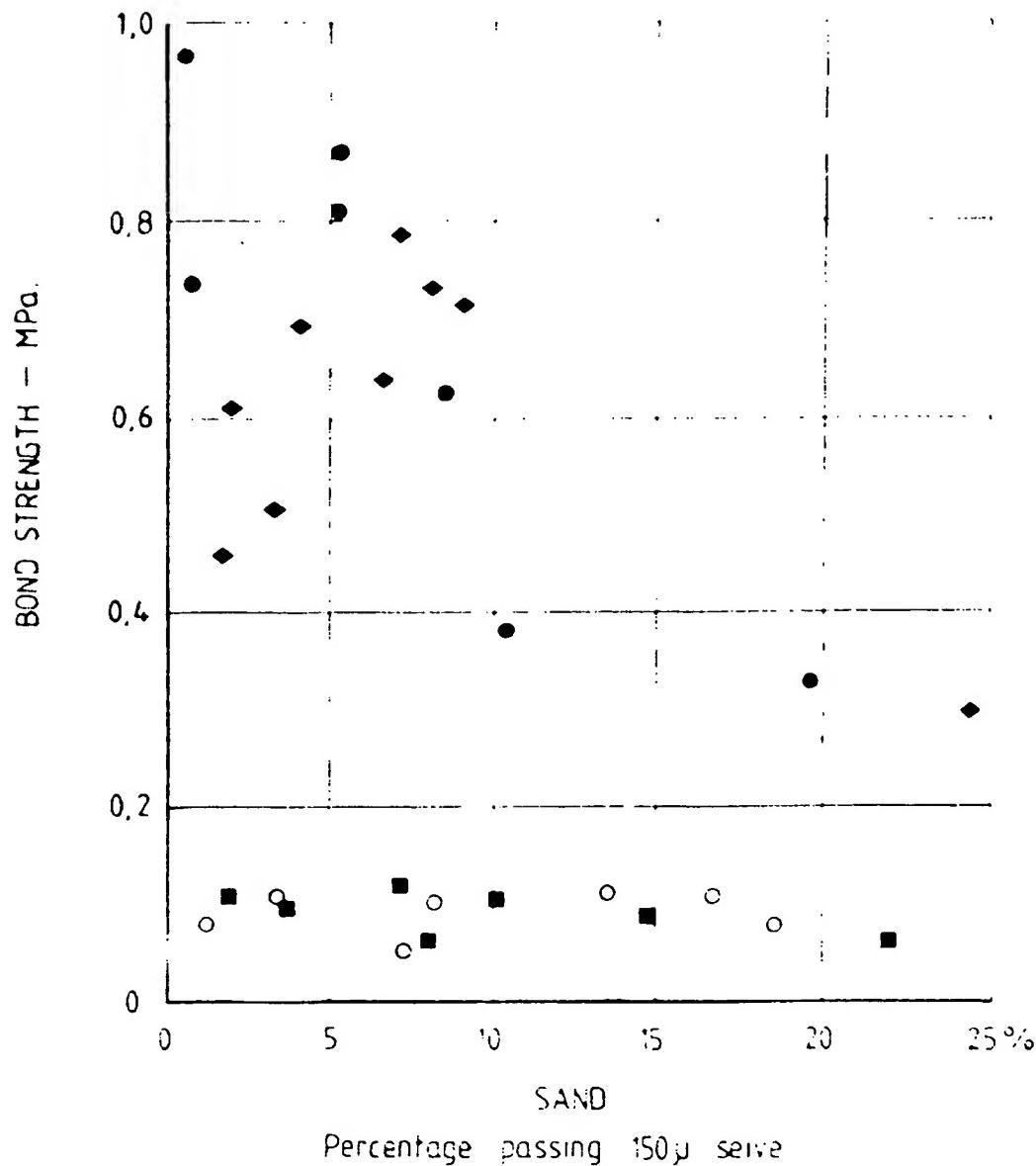


FIG. 2
AVERAGE BOND STRENGTH Vs. FINES

MIX:

- 1 Portland Cement : 5 Sand
 - 0.003 Parts by weight of modifier of Example 1
- ◆ Bricks
- Concrete Blocks
- Bricks (no modifier added to mortar)
- Concrete Blocks (no modifier added to mortar)



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